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ULTRAVIOLET ABSORPTION SPECTRA OF 4—CHLOROPYRIDINE VAPOUR

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The near ultraviolet absorption spectrum of 3-chloropyridine vapour having been obtained (Pandey 1967) by the author that of 4-chloropyridine vapour was also photographed to study the changes expected to arise as a result of change of the position 3 of chlorine to 4. Green's (1963) infrared and Raman data of this molecule have been used in support of the assignments proposed.

The system of bands obtained may be taken to appear due to $B_2 \leftarrow A_1$ electronic transition corresponding to the $B_{2u} \leftarrow A_{1g}$ of benzene. The strongest band at 36455 cm $^{-1}$ has been taken to be the 0—0 band. This is shifted by 1895 cm^{-1} to red with respect to the 0–0 band of the corresponding system of pyridine (38350 cm^{-1}). The red shifts of the 0–0 bands of the corresponding system of 2 and 3 bromopyridines are 1392 cm^{-1} and 2050 cm^{-1} respectively. These values reveal that the red shifts for the three isomers are in the order $3 > 2 > 4$. The electronic charge distribution at the different carbon positions in pyridine has been found to be like figure 1 (Coulson 1961). Hence the inductive effect for the three isomeric halogen substitutions should be in the order $4 > 2 > 3$. These results give support to the assignment of the 0—0 band.

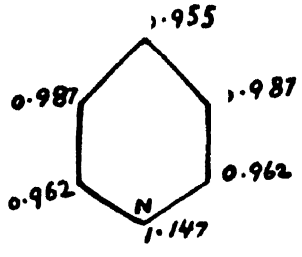

Fig. 1.

Because of N in the ring of chloropyridines, C—Cl bond in 3- Chloropyridines should be stronger than that in 4-Chloropyridines. Also the different amount of interaction of N with Cl should cause stronger C—C bond in 4-Chloropyridines as compared to that in 3-Chloropyridine. Along with intensity and combinability these interactions also have been taken into account while making assignment of observed bands as shown in the following table :

Table 1

Correlation and mode assignment of the frequencies observed in the spectra of 4-chloropyridine

Raman cm^{-1} (Green)	Infrared cm^{-1} (Green)	Ultraviolet		Assignment	Mode
		Ground State cm^{-1}	Excited State cm^{-1}		
182	—	183	145	δ(C—Cl)b_1	(16b)
—	—	336	253	β(C—Cl)b_2	—
415	414	409	—	β(C—C)a_1	6a
495	491	492	—	δ(C—C)a_2	16a(11)
663	663	653	—	β(C—C)b_2	6b
712	712	714	660	ν(C—Cl)a_1	(12)
—	—	789	—	ν(C—C)a_1	1
—	836	840	—	δ(C—H)a_2	10a(5)
—	—	1014	—	β(C—C)a_1	12
1103	1103	1106	1055	β(C—H)b_2	9a(18b)
1412	1407	—	1203	ν(C—C)b_2	19b

ν = stretching, β = in plane bending, δ = out of plane bending. Green's mode assignments which are different from those proposed here have been given in parentheses.

The author is thankful to Dr. D. Sharma, Professor and Head of the Department of Physics, Gorakhpur University, for supervision of this work.

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